On the use of the group SO(4,2) in atomic and molecular physics

Maurice R. Kibler

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by M. R. KIBLER

Institut de Physique Nucléaire de Lyon,

IN2P3-CNRS et Université Claude Bernard,

43 Boulevard du 11 Novembre 1918,

F-69622 Villeurbanne Cedex, France

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Abstract

In this paper the dynamical noninvariance group $\mathrm{SO}(4,2)$ for a hydrogen-like atom is derived through two different approaches. The first one is by an established traditional ascent process starting from the symmetry group $\mathrm{SO}(3)$. This approach is presented in a mathematically oriented original way with a special emphasis on maximally superintegrable systems, N-dimensional extension and little groups. The second approach is by a new symmetry descent process starting from the noninvariance dynamical group $\mathrm{Sp}(8,\mathbf{R})$ for a four-dimensional harmonic oscillator. It is based on the little known concept of a Lie algebra under constraints and corresponds in some sense to a symmetry breaking mechanism. This paper ends with a brief discussion of the interest of $\mathrm{SO}(4,2)$ for a new group-theoretical approach to the periodic table of chemical elements. In this connection, a general ongoing programme based on the use of a complete set of commuting operators is briefly described. It is believed that the present paper could be useful not only to the atomic and molecular community but also to people working in theoretical and mathematical physics.

1. INTRODUCTION

Professor Brian Garner Wybourne held a central place in the theoretical studies of atomic, molecular and condensed matter physics. His untimely death in November 2003 in Toruń, Poland, came as a shock to the scientific community.

Brian was an inspirational teacher who contributed significantly to the applications of symmetry in physics and chemical physics via the development of methods and models. He published part of his work on group theory and rare earth ions in crystals in three celebrated books [1-3]. He was active in many other fields (partly described in this Special Issue) either alone or in collaboration with many students and colleagues. The present author personally benefited enormously from Brian's work particularly in the following areas.

- Crystal-field theory (energy level calculation; relativistic crystal-field theory; intensity of electronic transitions between levels of partly-filled shell ions in solid-state or molecular environments).

- Group-theoretical methods in physics (through the use of characters, plethysms and Schur functions).

- Wigner-Racah calculus for finite or compact groups (especially for groups of interest in atomic and molecular physics).

A part of this paper in memory of Brian Wybourne could be regarded as an appendix to the chapter 'Case Study II: The hydrogen atom' of the textbook 'Clas-

sical Groups for Physicists' that Brian published in 1974 [3]. One aim of the present author is to provide a bibliography of the many works on the quantum-mechanical treatment of the hydrogen atom that have appeared since 1974. The main body of the paper is devoted to the set up of the mathematical ingredients for an investigation of the periodic table in connection with dynamical groups for the Coulomb system and the harmonic oscillator system.

This paper is organized in the following way. In § 2, the familiar standard derivation (central to Wybourne's analysis) of the dynamical noninvariance group SO(4, 2) for a hydrogen-like atom is revisited in a mathematical language in coherence with the new developments of § 3. In § 3, the derivation of the group SO(4, 2) is obtained from a symmetry descent process rather than by a symmetry ascent process. The originality of the latter derivation is to be found in the use of the mathematical concept of a Lie algebra under constraints developed by the present author and some of his collaborators. In the closing § 4, the interest of the group SO(4, 2) for a new group-theoretical description of the periodical charts for atoms, ions and molecules is touched upon and the general lines of an ongoing programme for a phenomenological although quantitative approach to the periodic table are given.

2. FROM SO(3) TO SO(4, 2)

A part of this section is devoted to a mathematical reformulation of known results

contained in Wybourne's book [3] in order to prepare the ingredients necessary for § 3 and § 4.

2.1 The chain SO(3) ⊂ SO(4)

Let

$$H\Psi = E\Psi \tag{1}$$

be the Schrödinger equation for a hydrogen-like atom of nuclear charge Ze ($Z = 1$ for hydrogen). We recall that the discrete spectrum ($E < 0$) of the nonrelativistic Hamiltonian H (in $N = 3$ dimensions) is given by

$$E \equiv E_3(n) = \frac{1}{n^2}\, E_3(1), \quad \Psi \equiv \Psi_{nlm}, \tag{2}$$

where $E_3(1)$ (with $E_3(1) < 0$) is the energy of the ground state (depending on the reduced mass of the hydrogen-like system, the nuclear charge and the Planck constant) and where

$$n = 1, 2, 3, \cdots$$

$$\text{for fixed } n : l = 0, 1, \cdots, n-1$$

$$\text{for fixed } l : m = -l, -l+1, \cdots, l. \tag{3}$$

The degeneracy degree of the level E_n is

$$d_3(n) = n^2 \tag{4}$$

if the spin of the electron is not taken into account ($2n^2$ if taken into account).

For fixed n and fixed l, the degeneracy of the $2l+1$ wavefunctions Ψ_{nlm} corresponding to different values of m (for $l \neq 0$) is explained by the three-dimensional proper rotation group, isomorphic to SO(3). The degeneracy in m follows from the existence of a first constant of the motion, i.e., the angular momentum $\mathbf{L}(L_1, L_2, L_3)$ of the electron of the hydrogen-like atom. Indeed, we have a first set of three commuting operators: the Hamiltonian H, the square $\mathbf{L}^2$ of the angular momentum of the electron and the third component L_3 of the angular momentum. The operators L_1, L_2 and L_3 span the Lie algebra of SO(3).

For fixed n, the degeneracy of the n^2 wavefunctions Ψ_{nlm} corresponding to different values of l (for $n \neq 1$) is accidental with respect to SO(3) and can be explained via the group SO(4), locally isomorphic to SU(2)$\otimes$SU(2). The introduction of SO(4) can be achieved in the framework either of a local approach credited to Pauli [4] (see also [5]) or a stereographic approach due to Fock [6]. We shall follow here the local or Lie-like approach developed by Pauli [4]. The degeneracy in l (for $n \neq 1$) follows from the existence of a second constant of the motion, i.e., the Runge-Lenz vector $\mathbf{M}(M_1, M_2, M_3)$ (discussed by Laplace, Hamilton, Runge and Lenz in classical mechanics and by Pauli in quantum mechanics). By properly rescaling the vector $\mathbf{M}$, we obtain a vector $\mathbf{A}(A_1, A_2, A_3)$ which has the dimension of an angular momentum. It can be shown that the set $\{L_i, A_i : i = 1, 2, 3\}$ spans the Lie algebra

of SO(4), SO(3, 1) and E(3) for $E < 0$, $E > 0$ and $E = 0$, respectively. As a point of fact, the obtained Lie algebras are Lie algebras with constraints since there exists two quadratic relations between $\mathbf{L}$ and $\mathbf{A}$ [4]. We now continue with the discrete spectrum corresponding to the case $E < 0$. Then, by defining

$$\mathbf{J} = \frac{1}{2}(\mathbf{L} + \mathbf{A}), \quad \mathbf{K} = \frac{1}{2}(\mathbf{L} - \mathbf{A}), \tag{5}$$

it is possible to write the Lie algebra of SO(4) in the form of the Lie algebra of the direct product $\mathrm{SO}(3)_J \otimes \mathrm{SO}(3)_K$ with the sets

$$\left\{ J_i = \frac{1}{2}(L_i + A_i) : i = 1, 2, 3 \right\}, \quad \left\{ K_i = \frac{1}{2}(L_i - A_i) : i = 1, 2, 3 \right\} \tag{6}$$

generating $\mathrm{SO}(3)_J$ and $\mathrm{SO}(3)_K$, respectively. The unitary irreducible representations (UIR's) of SO(4) can be labelled as (j, k) with $2j \in \mathbf{N}$ and $2k \in \mathbf{N}$. For fixed n, the n^2 functions Ψ_{nlm} generate the UIR $((n-1)/2, (n-1)/2)$ of SO(4), of dimension n^2, corresponding to $2j = 2k = n - 1$. The condition $j = k$ comes from one of the two quadratic relations between $\mathbf{L}$ and $\mathbf{A}$ (the condition $j = k$ corresponds to $\mathbf{J}^2 = \mathbf{K}^2$ in terms of $\mathbf{J}$ and $\mathbf{K}$). The other relation gives $E = E_3(1)/n^2$. Finally, note that the restriction from SO(4) to SO(3) yields the decomposition

$$\left(\frac{n-1}{2}, \frac{n-1}{2} \right) = (0) \oplus (1) \oplus \cdots \oplus (n-1) \tag{7}$$

in terms of UIR's (l) of SO(3).

Similar developments can be achieved (along the line of the local approach) for the continuum spectrum corresponding to the case $E > 0$ and for the zero-energy

point corresponding to the case $E = 0$. This leads to the Lorentz group in $3 + 1$ dimensions SO(3, 1) for $E > 0$ and to the Euclidean group in $N = 3$ dimensions $E(3)$ for $E = 0$. The two latter groups can also be obtained by means of a stereographic projection from $\mathbf{R}^4$ to $\mathbf{R}^3$ (along the line of the global approach) (see Ref. [7] for SO(3, 1)).

At this point, it is interesting to understand the different status of the groups SO(3), from one side, and SO(4), SO(3, 1) and E(3), from the other side, for a hydrogen-like atom. The special real orthogonal group SO(4), respectively SO(3), describes multiplets characterized by a given value of the principal quantum number n, respectively the orbital angular quantum number l; the multiplet of SO(4), respectively SO(3), associated with n, respectively l, is of dimension n^2, respectively $2l+1$. The compact group SO(3) is a geometrical symmetry group in the sense that it leaves invariant both the kinetic part and the potential part of the Hamiltonian H. As a consequence, the three generators L_i $(i = 1, 2, 3)$ of SO(3) commute with H. Hence, we have the set $\{H, \mathbf{L}^2, L_3\}$ of commuting operators. The compact group SO(4) is a dynamical invariance group that manifests itself here via its Lie algebra. The set of the bound state vectors associated with an arbitrary energy level of H spans a finite-dimensional UIR of SO(4). The group SO(4) does not correspond to a geometrical symmetry group of H but its six generators J_i and K_i $(i = 1, 2, 3)$ commute with H. Hence, we have the set $\{H, \mathbf{L}^2, L_3, \mathbf{A}^2, A_3\}$ of commuting opera-

tors. The latter set comprises five independent constants of the motion (the number $2N-1=5$ is the maximum number that we can have for a dynamical system in $N=3$ dimensions) so that the hydrogen-like system is a maximally superintegrable system. Similarly, we may think of the noncompact groups SO(3, 1) and E(3) as dynamical invariance groups.

Besides the symmetry group SO(3) and the three dynamical invariance groups SO(4), SO(3, 1) and E(3), another group, namely SO(4, 2), the special real pseudo-orthogonal group in $\mathbf{R}^{4,2}$, plays an important rôle. This group is locally isomorphic to SU(2, 2), the special unitary group in $\mathbf{C}^{2,2}$. It can be realized as a group of conformal transformations of the ordinary Minkowski space-time; this yields the conformal group (involving three space rotations, three space-time rotations, four space-time translations, one dilatation and four special conformal transformations) that is the most general group leaving invariant the Maxwell equations. The group SO(4, 2) was introduced, in connection with the hydrogen atom, by Malkin and Man'ko [8], in a $\mathrm{SO}(6,\mathbf{C})$ form, and independently by Barut and Kleinert [9] (see also Refs. [10] and [11]). The group SO(4, 2) is a dynamical noninvariance group in the sense that not all the generators of SO(4, 2) commute with H. It can be considered as a spectrum generating group since any wavefunction Ψ_{nlm} can be deduced from any other wavefunction through the action on Ψ_{nlm} of generators of SO(4, 2) which do not commute with H. Indeed, the group SO(4, 2) can serve for

describing the complete spectrum (including the discrete case, the continuum case and the zero-energy case) of a hydrogen-like atom. The bound state vectors and the continuum state vectors of a hydrogen-like atom can be classified by means of representations of the noncompact group SO(4, 2). For example, the infinite set

$$\{\Psi_{nlm} : n \in \mathbf{N}^*; l = 0, 1, \cdots, n-1; m = -l, -l+1, \cdots, l\} \tag{8}$$

of bound state vectors generates an infinite-dimensional UIR, noted h, of SO(4, 2). In other words, we have

$$h = (0, 0) \oplus (1/2, 1/2) \oplus (1, 1) \oplus \cdots. \tag{9}$$

This representation remains irreducible when restricting SO(4, 2) to its noncompact subgroup SO(4, 1). Therefore, the group SO(4, 1) is another dynamical noninvariance group for a hydrogen-like atom: the various bound state vectors of the Hamiltonian H can be connected owing to shift operators of SO(4, 1). Another relevant subgroup of SO(4, 2) is the noncompact group SO(3, 2). It is also a dynamical noninvariance group useful for describing the bound state and continuum state vectors of H. For instance, the set of the continuum state vectors spans an infinite-dimensional UIR of SO(3, 2). In addition, the bound state vectors with $n + l$ even (respectively, $n + l$ odd) span an infinite-dimensional UIR h_e (respectively, h_o) of SO(3, 2) and the restriction from SO(4, 2) to SO(3, 2) yields

$$h = h_o \oplus h_e. \tag{10}$$

The two de Sitter groups SO(3, 2) and SO(4, 1) can thus be considered as spectrum generating groups for a hydrogen-like system.

Most of what preceeds can be extended from $N = 3$ to N arbitrary with $N \geq 2$ [12-14]. This leads to a hydrogen-like atom in N dimensions described by a N-dimensional Schrödinger equation with an attractive N-dimensional Coulomb potential. The geometrical symmetry group for such a dynamical system is the rotation group in the space $\mathbf{R}^N$, a group isomorphic to SO(N). The spectrum for the energy E of this system has a discrete part ($E < 0$), a continuous part ($E > 0$) and a zero-energy point ($E = 0$). For the discrete part, the levels of energy $E_N(n)$ are characterized by a positive integer n. They are given by

$$E \equiv E_N(n) = \frac{(N-1)^2}{(2n+N-3)^2} E_N(1), \quad n \in \mathbf{N}^*, \tag{11}$$

where $E_N(1)$ (with $E_N(1) < 0$) is the energy of the ground level corresponding to $n = 1$. The degree of degeneracy $d_N(n)$ of the energy level $E_N(n)$ is

$$d_N(n) = \frac{(2n+N-3)(n+N-3)!}{(n-1)!(N-1)!} \tag{12}$$

(if the spin is not taken into consideration). For n arbitrary in $\mathbf{N}^*$, the degeneracy of the $d_N(n)$ state vectors (corresponding to $E < 0$) associated with the level $E_N(n)$ follows from the dynamical invariance group SO($N + 1$), a group isomorphic to the rotation group in the space $\mathbf{R}^{N+1}$. The group SO($N, 1$), a group isomorphic to a (spherical and hyperbolic) rotation group in the space $\mathbf{R}^{N,1}$, is a dynamical invari-

ance group for the continuum state vectors (corresponding to $E > 0$). Furthermore, the Euclidean group in N dimensions E(N), spanned by rotations and translations in the space $\mathbf{R}^N$, is a dynamical invariance group for the zero-energy state vectors (corresponding to $E = 0$). It should be noted that the groups SO($N+1$), SO($N,1$) and E(N) are the so-called *little groups* of the Poincaré group in a Minkowski space in $(N+1,1)$ dimensions. Finally, when passing from $N = 3$ to N arbitrary, the dynamical noninvariance group SO$(4,2)$ is replaced by SO$(N+1,2)$.

Going back to the case $N = 3$, which is of central importance for this work, we now give the general lines for constructing SO$(4,2)$ from SO(4) by an ascent process (cf. Refs. [3], [9], [15] and [16]). The presentation adopted here is based on Jordan-Schwinger calculus and is adapted to the developments in § 3.

2.2 The chain SO(4) $\subset$ SO$(4,2)$

The starting point is to find a bosonic realization of the Lie algebra of SO(4). Since SO(4) $\sim$ SU(2)$\otimes$SU(2)/Z_2, we can use twice the Jordan-Schwinger bosonisation of SU(2) [17]. Let us introduce two commuting pairs of boson operators (a_1, a_2) and (a_3, a_4). They satisfy the commutation relations

$$[a_i, a_j^\dagger] = \delta(i,j), \quad [a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0, \tag{13}$$

where the indices i, j can take the values 1 to 4 and where we use $A^\dagger$ to denote the Hermitean conjugate of the operator A. The a_i's are annihilation operators and the

$a_i^\dagger$'s are creation operators. It is a simple matter of calculation to check that the six bilinear forms (J_{12}, J_{23}, J_{31}) and (J_{14}, J_{24}, J_{34}) defined via

$$J_{ab} = \frac{1}{2}(\mathbf{a}^\dagger \, \sigma_c \, \mathbf{a} + \mathbf{b}^\dagger \, \sigma_c \, \mathbf{b}) \quad \text{with} \quad a, b, c \quad \text{cyclic} \tag{14a}$$

and

$$J_{a4} = -\frac{1}{2}(\mathbf{a}^\dagger \, \sigma_a \, \mathbf{a} - \mathbf{b}^\dagger \, \sigma_a \, \mathbf{b}) \tag{14b}$$

span the Lie algebra D_2 of SO(4). In the latter two definitions, we have

- the indices a, b, c can take the values 1 to 3

- σ_1, σ_2 and σ_3 are the three Pauli matrices

- $\mathbf{a}$ and $\mathbf{b}$ stand for the column vectors whose transposed vectors are the line vectors ${}^t\mathbf{a} = (a_1 a_2)$ and ${}^t\mathbf{b} = (a_3 a_4)$, respectively

- $\mathbf{a}^\dagger$ and $\mathbf{b}^\dagger$ stand for the line vectors $\mathbf{a}^\dagger = (a_1^\dagger a_2^\dagger)$ and $\mathbf{b}^\dagger = (a_3^\dagger a_4^\dagger)$, respectively.

We can find nine additional operators which together with the two triplets of operators (J_{12}, J_{23}, J_{31}) and (J_{14}, J_{24}, J_{34}) generate the Lie algebra D_3 of SO(4, 2). These generators can be defined as

$$J_{a5} = i[J_{a4}, J_{45}] \quad \text{with} \quad a = 1, 2, 3,$$

$$J_{45} = \frac{1}{2}(\mathbf{a}^\dagger \, \sigma_2 \, {}^t\mathbf{b}^\dagger - \mathbf{a} \, \sigma_2 \, {}^t\mathbf{b}),$$

$$J_{a6} = -i[J_{a5}, J_{56}] \quad \text{with} \quad a = 1, 2, 3,$$

$$J_{46} = -i[J_{45}, J_{56}],$$

$$J_{56} = \frac{1}{2}(\mathbf{a}^\dagger \mathbf{a} + \mathbf{b}^\dagger \mathbf{b} + 2). \tag{15}$$

The fifteen operators (J_{12}, J_{23}, J_{31}), (J_{14}, J_{24}, J_{34}), on one hand, and $(J_{15}, J_{25}, J_{35}, J_{45})$, $(J_{16}, J_{26}, J_{36}, J_{46}, J_{56})$, on the other hand, can be shown to satisfy

$$[J_{ab}, J_{cd}] = i(g_{bc} J_{ad} - g_{ac} J_{bd} + g_{ad} J_{bc} - g_{bd} J_{ac}) \tag{16}$$

with the metric tensor (g_{ab}) defined by

$$(g_{ab}) = \mathrm{diag}(-1, -1, -1, -1, +1, +1), \tag{17}$$

where the indices a, b, c, d can take the values 1 to 6. We thus end up with the Lie algebra of $\mathrm{SO}(4, 2)$, a group which leaves the real quadratic form

$$-\sum_{a,b} g_{ab}\, x_a\, x_b = x_1^2 + x_2^2 + x_3^2 + x_4^2 - x_5^2 - x_6^2 \tag{18}$$

invariant. A set of infinitesimal generators of $\mathrm{SO}(4, 2)$, acting on functions $f : (x_1, x_2, \cdots, x_6) \mapsto f(x_1, x_2, \cdots, x_6)$ of six variables, is provided by the differential operators

$$J_{ab} \mapsto U_{ab} = i \left(g_{aa}\, x_a\, \frac{\partial}{\partial x_b} - g_{bb}\, x_b\, \frac{\partial}{\partial x_a} \right) \tag{19}$$

which generalize the components of the usual orbital angular momentum in the ordinary space $\mathbf{R}^3$.

Since the Lie algebra of $\mathrm{SO}(4, 2)$ is of rank 3, we have three invariant operators in its enveloping algebra. Indeed, they are of degree 2, 3 and 4 and are given by

$$C_1 = \sum J_{ab} J^{ab},$$

$$C_2 = \sum \epsilon_{abcdef} J^{ab} J^{cd} J^{ef},$$

$$C_3 = \sum J_{ab} J^{bc} J_{cd} J^{da}, \tag{20}$$

where ϵ is the totally anti-symmetric tensor on six covariant indices with $\epsilon_{123456} = 1$ and

$$J^{ab} = \sum g^{ac}\, g^{bd}\, J_{cd} \quad \text{with} \quad g^{ab} = g_{ab}, \tag{21}$$

where we use the Einstein summation conventions.

We now briefly discuss the existence of the special representation h of SO$(4,2)$ that provides the quantum numbers n, l and m. It can be seen that the operator J_{45} connects states having different values of n. This clearly shows that the Lie algebra of the group SO$(4,2)$ is a dynamical noninvariance algebra. In fact, it is possible to construct any state vector Ψ_{nlm} by repeated application on the ground state vector Ψ_{100} of the operator $J_{45} - J_{46}$ and of shift operators for SO(4). This result is at the root of the fact that all discrete levels (or bound states) of a hydrogen-like atom span an UIR of SO$(4,2)$. This is the representation h discussed above. It corresponds to the eigenvalues 6, 0 and -12 of the invariant operators C_1, C_2 and C_3, respectively. The dynamical noninvariance group SO$(4,2)$ contains the dynamical noninvariance group SO$(4,1)$ that contains in turn the dynamical invariance group SO(4) and thus the geometrical symmetry group SO(3). The restriction of SO$(4,2)$ to SO(4) yields

the decomposition

$$h = \bigoplus_{n \in \mathbf{N}^*} \left(\frac{n-1}{2}, \frac{n-1}{2} \right) \tag{22}$$

which is a direct sum of the representations (j, j), with $2j \in \mathbf{N}$, of the group SO(4). Further restriction from SO(4) to SO(3) gives

$$h = \bigoplus_{n=1}^{\infty} \bigoplus_{l=0}^{n-1} (l) \tag{23}$$

that reflects that all the discrete states (with $E < 0$) of a hydrogen-like atom are contained in a single UIR of $\mathrm{SO}(4, 2)$. A similar result holds for the continuum states (with $E > 0$).

3. FROM $\mathrm{Sp}(8, \mathbf{R})$ TO $\mathrm{SO}(4, 2)$

3.1 Two important dynamical systems

The hydrogen atom and the harmonic oscillator are two dynamical systems of paramount importance for nuclear, atomic and molecular physics. The harmonic oscillator turns out to be a corner-stone in nuclear spectroscopy, molecular dynamics and the theory of radiation while the hydrogen atom is of considerable importance in the theory of atomic and molecular structure. They can be considered as two paradigms among the exactly solvable dynamical systems. In fact, hydrogen-like atoms are the sole atoms for which we know how to solve exactly the Schrödinger equation. (In passing, let us remember that hydrogen constitutes the 3/4 of the

known universe.) From the point of view of classical mechanics, each of these two systems (in $N = 3$ dimensions) corresponds to the motion of a particle in an attractive spherically symmetric potential (the Coulomb potential and the isotropic harmonic oscillator potential) for which the bounded trajectories are closed [18] (the case of the hydrogen atom being associated with the Kepler motion). In addition, the two systems (both from a classical and a quantum-mechanical aspect) are maximally superintegrable systems with $2N - 1 = 5$ constants of the motion (see for example Ref. [19]).

A connection between the hydrogen atom and the isotropic harmonic oscillator has been recognized for a long time by numerous authors [20-42]. Such a connection can be established via Lie-like methods (local or infinitesimal approach) or algebraic methods based on nonbijective canonical transformations (global or partial differential equation approach). From these two approaches, to be described below, it is possible to derive the dynamical noninvariance group $\mathrm{SO}(4, 2)$ for a hydrogen-like atom in $N = 3$ dimensions from the dynamical noninvariance group $\mathrm{Sp}(8, \mathbf{R})$ for an isotropic harmonic oscillator in $N = 4$ dimensions. This will be done in § 3.4 in an original way.

3.2 The global approach

It is based on the Kustaanheimo-Stiefel transformation introduced in celestial

mechanics for regularizing the Kepler problem [22, 23]. This transformation is the $\mathbf{R}^4 \to \mathbf{R}^3 : (u_1, u_2, u_3, u_4) \mapsto (x_1, x_2, x_3)$ surjection defined by

$$x_1 = 2(u_1 u_3 - u_2 u_4),$$

$$x_2 = 2(u_1 u_4 + u_2 u_3),$$

$$x_3 = u_1^2 + u_2^2 - u_3^2 - u_4^2), \tag{24a}$$

accompanied by the constraint

$$-u_1 du_2 + u_2 du_1 + u_3 du_4 - u_4 du_3 = 0. \tag{24b}$$

This nonbijective canonical transformation can be identified with the Hopf fibration $\mathrm{S}^3 \times \mathbf{R}_+ \to \mathrm{S}^2 \times \mathbf{R}_+$ with compact fiber S^1 and can be introduced in a natural way through the theory of spinors [39-41].

The application of the Kustaanheimo-Stiefel transformation to the Schrödinger equation $H\Psi = E\Psi$ for a hydrogen-like atom (in $N = 3$ dimensions) leads to a Schrödinger equation for an isotropic harmonic oscillator in $N = 4$ dimensions subjected to a constraint [27-30, 32-38]. In Ref. [35], it was shown that the Schrödinger equation for the oscillator is amenable to a system of Schrödinger equations for

- a pair of two-dimensional isotropic harmonic oscillators with attractive potentials and subjected to a constraint in the case $E < 0$,

- a pair of two-dimensional isotropic harmonic oscillators with repulsive potentials and subjected to a constraint in the case $E > 0$,

- a pair of two-dimensional free particle systems subjected to a constraint in the case $E = 0$.

3.3 The local approach

The result just enunciated can be also obtained by combining the Pauli approach [4] of a hydrogen-like atom with the Schwinger approach [17] of angular momentum. By way of illustration, we consider the case $E < 0$. In that case, the noninvariance dynamical algebra of the Lie group SO(4) can be converted into the Lie algebra of the group SU(2)$\otimes$SU(2) with a constraint. According to Schwinger [17], each group SU(2) which describes a generalized angular momentum can be associated with a two-dimensional isotropic harmonic oscillator. We are thus left with the following result: The discrete spectrum (corresponding to $E < 0$) for a hydrogen-like atom can be deduced from the quantization of a pair of three-dimensional generalized angular momenta with constraint or alternatively a pair of two-dimensional isotropic harmonic oscillators with attactive potentials and having the same energy. Similar results hold for $E > 0$ and $E = 0$.

3.4 Connecting the dynamical noninvariance algebras

We are now in a position to derive in a very simple way the dynamical noninvariance group SO$(4, 2)$ for a hydrogen-like atom.

At this stage, we have to recall that the dynamical noninvariance group for the

isotropic harmonic oscillator in N dimemensions ($N \geq 1$) is the real symplectic group $\mathrm{Sp}(2N, \mathbf{R})$ [43-49]. This noncompact group admits the group $\mathrm{SU}(N)$ as a maximal compact subgroup. The latter subgroup is the dynamical invariance group for the N-dimensional oscillator with attractive potential [43-45]. This dynamical system presents the energy levels

$$F_N(n) = \frac{2n+N}{N} F_N(0), \quad n \in \mathbf{N}, \tag{25}$$

where $F_N(0)$ (with $F_N(0) > 0$) stands for the energy of the ground level corresponding to $n = 0$. The degree of degeneracy $e_N(n)$ of the energy level $F_N(n)$ is

$$e_N(n) = \frac{(n+N-1)!}{n!(N-1)!}. \tag{26}$$

We are interested here in the situation where $N = 4$ and therefore with the group $\mathrm{Sp}(8, \mathbf{R})$ as the dynamical noninvariance group for a four-dimensional isotropic harmonic oscillator. As a remarkable result, the constraint for $E < 0$, $E > 0$ and $E = 0$ assumes the same form and amounts to take as zero one of the thirty-six generators of $\mathrm{Sp}(8, \mathbf{R})$. This produces a Lie algebra under constraints that is isomorphic to the Lie algebra of $\mathrm{SO}(4, 2)$. An original derivation of central importance for the future developments of § 4 is in order.

The constraint Cartan 1-form defined by Eq. (24b) gives rise to a vector field which can be seen to belong to the Lie algebra of $\mathrm{Sp}(8, \mathbf{R})$. This vector field generates a one-dimensional Lie algebra isomorphic to the Lie subalgebra of a subgroup $\mathrm{SO}(2)$

of $\mathrm{Sp}(8,\mathbf{R})$. Then, the dynamical noninvariance group for the hydrogen-like results from the vanishing of the vector field under consideration inside the Lie algebra of $\mathrm{Sp}(8,\mathbf{R})$. This produces a Lie algebra under constraints that can be derived as follows. According to the concept of Lie algebra under constraints [42], we have to find first the centraliser of the Lie algebra of SO(2) into the Lie algebra of $\mathrm{Sp}(8,\mathbf{R})$. We obtain

$$\mathrm{cent}_{\mathrm{sp}(8,\mathbf{R})}\mathrm{so}(2) = \mathrm{u}(2,2) \tag{27}$$

(we use lower case letters for Lie algebras). Then, the Lie algebra we are looking for is given by the factor algebra of this centralizer by so(2). We thus get

$$\mathrm{cent}_{\mathrm{sp}(8,\mathbf{R})}\mathrm{so}(2)/\mathrm{so}(2) = \mathrm{su}(2,2) \sim \mathrm{so}(4,2) \tag{28}$$

In simple terms, the Lie algebra so(4, 2) of the Lie group SO(4, 2) appears as the Lie algebra that survives when one forces the generator of SO(2) to vanish within the Lie algebra of $\mathrm{Sp}(8,\mathbf{R}) \supset \mathrm{SO}(2)$.

As a conclusion, the dynamical noninvariance algebra of the group $\mathrm{SO}(4,2)$ for a hydrogen-like atom in $\mathbf{R}^3$ was obtained from the dynamical noninvariance algebra of the group $\mathrm{Sp}(8,\mathbf{R})$ for an isotropic harmonic oscillator in $\mathbf{R}^4$. This derivation of $\mathrm{SO}(4,2)$ corresponds to a symmetry descent process and should be contrasted with the one in § 2.2 which corresponds to a symmetry ascent process. A link between the two derivations can be established by noting that the Lie algebra of $\mathrm{Sp}(8,\mathbf{R})$ can be

generated by the thirty-six possible bilinear forms constructed from the annihilation operators a_i and the creation operators $a_i^\dagger$ ($i = 1$ to 4) used in § 2.2 and that fifteen of these bilinear forms generate the Lie algebra of SU(2, 2), the covering group of SO(4, 2). When the vector field that generates SO(2) is written in terms of the annihilation and creation operators of Eq. (13), the Lie algebra given by Eq. (28) appears to be the one, up to canonical transformations, described by Eqs. (14) and (15).

4. APPLICATION TO PERIODIC CHARTS

To close this paper, we briefly discuss the use of the group SO(4, 2) for the classification of chemical elements. The importance of SO(4, 2) for the periodic charts of neutral atoms and ions was noted by Barut [50] during the Rutherford Centennial symposium organised by Wybourne at the University of Canterbury (New Zealand) in 1971 and, independently, by Rumer and Fet [51] (see also [52, 53]) in the former Soviet Union in 1971 too. Later, Byakov *et al.* [54] further developed this group-theoretical approach of the periodic chart of chemical elements by introducing the direct product SO(4, 2)⊗SU(2). One of the deep reasons for using SO(4, 2) relies upon the fact that the Madelung rule inherent to the *Aufbau Prinzip* can be described by the representation h of SO(4, 2) [50, 55, 56].

In the *à la* SO(4, 2) or SO(4, 2)⊗SU(2) approach to the periodic table, the

infinite-dimensional UIR h of SO(4, 2) is used for describing neutral atoms. Each atom thus appears as a particular partner for the representation $h \otimes [2]$ of the group SO(4, 2)⊗SU(2) where [2] stands for the fundamental represention of SU(2). In fact, it is possible to connect two partners of the representation $h \otimes [2]$ by making use of shift operators of the Lie algebra of SO(4, 2)⊗SU(2). In other words, it is possible to pass from one atom to another one by means of raising or lowering operators. We thus obtain a chart with rows and columns for which the nth row contains $2n^2$ elements and the lth column contains an infinite number of elements. A given column corresponds to a family of chemical analogs in the standard periodic table and a given row may contain several periods of the standard periodic table. Three features of the SO(4, 2)⊗SU(2) periodic table are the following: (i) hydrogen is in the family of the alkali metals, (ii) helium belongs to the family of the alkaline earth metals, and (iii) the inner transition series (lanthanides and actinides) as well as the transition series (iron group, palladium group and platinum group) occupy a natural place in the table. This is to be contrasted with the conventional tables with 8(9) or 18 columns where: (i) hydrogen is sometimes located in the family of the halogens, (ii) helium generally belongs to the family of the noble gases, and (iii) the lanthanide series and the actinide series are generally treated as appendages. The reader may consult Ref. [56] for more details.

To date, the use of SO(4, 2) or SO(4, 2)⊗SU(2) in connection with periodic charts

has been limited to qualitative aspects only, viz., classification of neutral atoms and ions as well. We would like to give here the main lines of a programme under development (inherited from nuclear physics and particle physics) for dealing with quantitative aspects.

The first step concerns the mathematics of the programme. The direct product group $SO(4,2)\otimes SU(2)$ is a Lie group of order eighteen. Let us first consider the $SO(4,2)$ part which is a semi-simple Lie group of order $r = 15$ and of rank $l = 3$. It has thus fifteen generators involving three Cartan generators (i.e., generators commuting between themselves). Furthermore, it has three invariant operators or Casimir operators (i.e., independent polynomials, in the enveloping algebra of the Lie algebra of $SO(4,2)$, that commute with all generators of the group $SO(4,2)$). Therefore, we have a set of six $(3+3)$ operators that commute between themselves: the three Cartan generators and the three Casimir operators. Indeed, this set is not complete from the mathematical point of view. In other words, the eigenvalues of the six above-mentioned operators are not sufficient for labelling the state vectors in the representation space of $SO(4,2)$. According to a (not very well-known) result popularised by Racah, we need to find

$$\frac{1}{2}(r - 3l) = 3 \tag{29}$$

additional operators in order to complete the set of the six preceding operators. This yields a complete set of nine $(6+3)$ commuting operators and this solves the state

labelling problem for the group SO(4, 2). The consideration of the group SU(2) is trivial: SU(2) is a semi-simple Lie group of order $r = 3$ and of rank $l = 1$ so that $(r - 3l)/2 = 0$ in that case. As a result, we end up with a complete set of eleven $(9 + 2)$ commuting operators. It is to be stressed that this result constitutes the key and original starting point of the programme.

The second step establishes contact with chemical physics. Each of the eleven operators can be taken to be self-adjoint and thus, from the quantum-mechanical point of view, can describe an observable. Indeed, four of the eleven operators, namely, the three Casimir operators of SO(4, 2) and the Casimir operator of SU(2), serve for labelling the representation $h \otimes [2]$ of SO(4, 2)⊗SU(2) for which the various chemical elements are partners. The seven remaining operators can thus be used for describing chemical and physical properties of the elements like:

-ionization energies,

-electron affinities,

-electronegativities,

-melting and boiling points,

-specific heats,

-atomic radii,

-atomic volumes,

-densities,

-magnetic susceptibilities,

-solubilities, etc.

In most cases, this can be done by expressing a chemical observable associated with a given property in terms of the seven operators which serve as an integrity basis for the various observables. Each observable can be developed as a linear combination of operators constructed from the integrity basis. This is reminiscent of group-theoretical techniques used in nuclear and atomic spectroscopy (cf. the Interacting Boson Model) or in hadronic spectroscopy (cf. the Gell-Mann/Okubo mass formulas for baryons and mesons).

The last step is to proceed to a diagonalisation process and then to fit the various linear combinations to experimental data. This can be achieved through fitting procedures concerning either a period of elements (taken along a same line of the periodic table) or a family of elements (taken along a same column of the periodic table). For each property this will lead to a formula or phenomenological law that can be used in turn for making predictions concerning the chemical elements for which no data are available. In addition, it is hoped that this will shed light on the new patterns of the periodic table recently discovered; along this vein, the singularity principle, the diagonal relationships and the inert pair effect [57-59] are patterns that can be described on a mathematical basis by using ladder operators.

This programme, referred to as the KGR programme, was briefly presented at

the 2003 Harry Wiener International Conference [60]. It is presently under progress. The concept of q-deformation (as arising in the theory of quantum groups), already applied to the classification of atoms and ions [61, 62], is of potential interest for this programme. Finally, it should be emphasized that this programme might be adapted to molecules since subgroups of $SO(4,2)$ were successfully used for periodic systems of molecules [63, 64].

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